Surface-Induced Phase Transformations: Multiple Scale and Mechanics Effects and Morphological Transitions. Supplementary Material

Valery I. Levitas[1] and Mahdi Javanbakht[2]

[1]*Iowa State University, Departments of Mechanical Engineering, Aerospace Engineering, and Material Science and Engineering, Ames, Iowa 50011, USA*

[2]*Iowa State University, Department of Mechanical Engineering, Ames, Iowa 50011, USA*

We designate contractions of tensors $\boldsymbol{A} = \{A_{ij}\}$ and $\boldsymbol{B} = \{B_{ji}\}$ over one and two indices as $\boldsymbol{A}{\cdot}\boldsymbol{B} = \{A_{ij}\, B_{jk}\}$ and $\boldsymbol{A}{:}\boldsymbol{B} = A_{ij}\, B_{ji}$, respectively. The subscripts s, e, and t mean symmetrization and elastic and transformational strains; $\boldsymbol{I}$ is the unit tensor; $\overset{\circ}{\boldsymbol{\nabla}}$ and $\boldsymbol{\nabla}$ are the gradient operators in the undeformed and deformed states; $\otimes$ designates a dyadic product.

Phase-field model. The current model generalizes our recently developed model [1] by including the surface layer. Thus, an additional order parameter ξ describes a smooth transition between solid ($\xi = 0$) and surrounding ($\xi = 1$), e.g., gas. Additional energy term $\psi_\xi(\xi, \boldsymbol{\nabla}\xi, \eta_k)$ and GL equation for ξ are formulated to ensure coupling between different order parameters η_i and ξ in a consistent way. Kinematics relationships between displacement $\boldsymbol{u}$ and strain $\boldsymbol{\varepsilon} = 1/3\varepsilon_0 \boldsymbol{I} + \boldsymbol{e}$, decomposition of $\boldsymbol{\varepsilon}$ and the equilibrium equation are

$$\boldsymbol{\varepsilon} = (\overset{\circ}{\boldsymbol{\nabla}}\, \boldsymbol{u})_s, \quad \boldsymbol{\varepsilon} = \boldsymbol{\varepsilon}_e + \boldsymbol{\varepsilon}_t, \quad \boldsymbol{\nabla}\cdot\boldsymbol{\sigma} = 0, \tag{1}$$

where ε_0 and $\boldsymbol{e}$ are the volumetric and deviatoric contributions to strain, and $\boldsymbol{\sigma}$ is the true Cauchy stress tensor. The Helmholtz free energy per unit undeformed volume ψ and transformation strain tensor $\boldsymbol{\varepsilon}_t$ are accepted in the form

$$\psi = \psi^e(\varepsilon_0, \boldsymbol{e}, \eta_i, \theta, \xi) + \frac{\rho_0}{\rho}\breve{\psi}^\theta + \psi^\theta + \frac{\rho_0}{\rho}\psi^\nabla + \frac{\rho_0}{\rho}\psi_\xi(\xi, \boldsymbol{\nabla}\xi, \eta_k); \tag{2}$$

$$\psi^\theta = \sum_{k=1}^{n} \frac{1}{3} A_0(\theta - \theta_e)\phi(\eta_k) - \sum_{i=1}^{n-1}\sum_{j=i+1}^{n} \eta_i^2\eta_j^2(\eta_i + \eta_j) A_0(\theta - \theta_e); \tag{3}$$

$$\psi^\nabla = \frac{\beta}{2}\Big(\sum_{i=1}^{n} |\boldsymbol{\nabla}\eta_i|^2 + b\sum_{i=1}^{n}\sum_{j=1, i\neq j}^{n} \boldsymbol{\nabla}\eta_i \cdot \boldsymbol{\nabla}\eta_j\Big); \tag{4}$$

$$\breve{\psi}^\theta = \sum_{k=1}^{n} A_0(\theta_e - \theta_c)\eta_k^2(1 - \eta_k)^2 + \sum_{i=1}^{n-1}\sum_{j=i+1}^{n} F_{ij}(\eta_i, \eta_j); \tag{5}$$

$$\boldsymbol{\varepsilon}_t = \sum_{k=1}^{n} \boldsymbol{\varepsilon}_t^k (a\eta_k^2 + (4 - 2a)\eta_k^3 + (a - 3)\eta_k^4) - \sum_{i=1}^{n-1}\sum_{j=i+1}^{n} \eta_i^2\eta_j^2(\eta_i \boldsymbol{L}_{ij} + \eta_j \boldsymbol{L}_{ji}), \tag{6}$$

$$\psi^e = 0.5(1 - \phi(\xi))(K\varepsilon_{0e}^2 + 2\mu \boldsymbol{e}_e{:}\boldsymbol{e}_e); \quad \phi(\xi) = \xi^2(3 - 2\xi). \tag{7}$$

Here, $\frac{\rho_0}{\rho}=1+\varepsilon_0$ are the ratio of mass densities in the undeformed and deformed states, $\boldsymbol{L}_{ij}=(a-3)\boldsymbol{\varepsilon}_t^j+3\boldsymbol{\varepsilon}_t^i$, $F_{ij}(\eta_i,\eta_j)=\eta_i\eta_j(1-\eta_i-\eta_j)\{B[(\eta_i-\eta_j)^2-\eta_i-\eta_j]+C\eta_i\eta_j\}+\eta_i^2\eta_j^2(\eta_i+\eta_j)(\bar{A}-A_0(\theta_e-\theta_c))$, ψ^e is the elastic energy with equal (for compactness) bulk K and shear μ moduli of martensitic variants, which smoothly reduce to zero within the surface layer;

β is the gradient energy coefficient; and A_0, $\bar{A}$, B, C, a, and b are parameters. For the sharp external surface with the normal $\boldsymbol{n}$, the boundary conditions for the order parameters related to the variable surface energy $q(\eta_i)$ are defined as [1]

$$\frac{\rho}{\rho_0}\frac{\partial\psi}{\partial\boldsymbol{\nabla}\eta_i}\cdot\boldsymbol{n}=\frac{\partial\psi^\nabla}{\partial\boldsymbol{\nabla}\eta_i}\cdot\boldsymbol{n}=\beta(\nabla\eta_i+b\sum_{j=1,i\neq j}^{n}\boldsymbol{\nabla}\eta_j)\cdot\boldsymbol{n}=-\frac{\partial q}{\partial\eta_i};$$
$$q(\eta_i)=\gamma_A+\Delta\gamma\phi(p),\qquad p=(\eta_1^2+\eta_2^2+...+\eta_i^2+...)^{0.5},\tag{8}$$

where γ is the surface energy and $\Delta\gamma=\gamma_M-\gamma_A$. For the finite surface layer, the boundary conditions for η_i correspond to unchanged energy of external surface ($q=const$ in Eq.(8)).

Surface layer model. The energy of the surface layer per unit deformed volume is

$$\psi_\xi=J\xi^2(1-\xi)^2+0.5\beta_\xi(\nabla\xi)^2=q(\eta_i)/\Delta_\xi\left(16.62\xi^2(1-\xi)^2+0.542\Delta_\xi^2(\nabla\xi)^2\right).\tag{9}$$

Eqs.(2), (7), and (9) lead to the GL equations for ξ and η_i:

$$\frac{1}{L_\xi}\frac{\partial\xi}{\partial t}=\frac{q(\eta_i)}{\Delta_\xi}\left(1.083\Delta_\xi^2\nabla^2\xi-66.48\xi(1-\xi)(0.5-\xi)\right)-\frac{\rho}{\rho_0}\frac{\partial\psi^e}{\partial\xi};\tag{10}$$
$$\frac{1}{L}\frac{\partial\eta_i}{\partial t}=-\frac{\rho}{\rho_0}\frac{\partial\psi}{\partial\eta_i}|_{\boldsymbol{\varepsilon}}+\boldsymbol{\nabla}\cdot\left(\frac{\rho}{\rho_0}\frac{\partial\psi}{\partial\boldsymbol{\nabla}\eta_i}\right)=\frac{\rho}{\rho_0}\boldsymbol{\sigma}_e\boldsymbol{:}\frac{d\boldsymbol{\varepsilon}_t}{d\eta_i}-\frac{\rho}{\rho_0}\frac{\partial\psi^\theta}{\partial\eta_i}-\frac{\partial\breve{\psi}^\theta}{\partial\eta_i}$$
$$+\beta(\boldsymbol{\nabla}^2\eta_i+b\sum_{j=1,i\neq j}^{n}\boldsymbol{\nabla}^2\eta_j)-\frac{1}{\Delta_\xi}\frac{\partial q}{\partial\eta_i}\left(16.62\xi^2(1-\xi)^2+0.542\Delta_\xi^2(\nabla\xi)^2\right),\tag{11}$$

where L and $L_\xi\gg L$ are the kinetic coefficients and $\partial\psi/\partial\eta_i$ is calculated at $\boldsymbol{\varepsilon}=const$. We would like to avoid description of an actual solid-gas PT and want to develop a more generic model of the surface layer. That is why ψ_ξ has the same structure as $\breve{\psi}^\theta+\psi^\nabla$ for single order parameter η, with β_ξ for the gradient energy coefficient and J characterizing the double-well energy barrier. Since for homogeneous states $\psi_\xi(0)=\psi_\xi(1)=0$, Eq.(9) corresponds to the thermodynamic equilibrium between solid and surrounding. For neglected elastic energy, Eq.(10) has a stationary solution for an equilibrium surface layer [2]:

$$\xi=[1+\exp(5.54x/\Delta_\xi)]^{-1};\quad\Delta_\xi=5.54\sqrt{\beta_\xi/(2J)};\quad E_\xi=\sqrt{\beta_\xi J/18}=q(\eta_i).\tag{12}$$

Here the surface layer width is $\Delta_\xi=|x_g-x_s|$, and x_g and x_s are determined from the conditions $\phi(\xi(x))=0.01$ and 0.99 respectively; the surface-layer energy E_ξ should be equal to the variable surface energy $q(\eta_i)$ to make the surface layer and sharp surface approaches energetically equivalent. Assuming that Δ_ξ is independent of η_i, one obtains from Eq.(12) $\beta_\xi = \frac{6E_\xi \Delta_\xi}{5.54} = 1.083 q(\eta_i)\Delta_\xi$ and $J = \frac{16.62 q(\eta_i)}{\Delta_\xi}$, which justifies the second part of Eq.(9). For neglected mechanics, the stationary version of Eq.(10) and its solution are independent of η_i and 1-D solution Eq.(12) is valid during evolution of η_i as well. Since the magnitude of the local contribution of the surface layer to the GL for η (the last term in Eq.(11)) scales with $1/\Delta_\xi$, the driving force X_c that causes PT should increase with growing Δ_ξ, which is confirmed by numerical simulations (Fig. 1). When mechanics is taken into account but the last term in Eq.(10) is negligible, stationary distribution of η_i affects stationary distribution of ξ through a change in the size of the sample due to transformation strain. However, stationary distribution of ξ mapped into the undeformed state remains unchanged. For neglected ψ^e, Eq.(10) has solution for a stationary surface layer [2]: $\xi_s = [1 + \exp(5.54x/\Delta_\xi)]^{-1}$. For neglected mechanics and single stationary surface layer orthogonal to x, Eq.(11) simplifies to

$$\frac{1}{L}\frac{\partial \eta_i}{\partial t} = -\frac{\partial(\breve{\psi}^\theta + \psi^\theta)}{\partial \eta_i} + \beta \boldsymbol{\nabla}^2 \eta_i - \frac{33.24}{\Delta_\xi}\frac{\partial q(\eta_i)}{\partial \eta_i}\xi_s^2 (1-\xi_s)^2,$$

where we took into account that for the stationary solution ξ_s the local and gradient terms in the energy Eq.(9) are equal [3].

Stresses in [1] are supplemented by the term due to ξ-related surface stresses $\boldsymbol{\sigma}_\xi^{st}$:

$$\boldsymbol{\sigma} = \frac{\rho}{\rho_0}\frac{\partial \psi}{\partial \boldsymbol{\varepsilon}} - \sum_{i=1}^{n}\frac{\rho}{\rho_0}\left(\boldsymbol{\nabla}\eta_i \otimes \frac{\partial \psi}{\partial \boldsymbol{\nabla}\eta_i}\right)_s - \frac{\rho}{\rho_0}\left(\boldsymbol{\nabla}\xi \otimes \frac{\partial \psi}{\partial \boldsymbol{\nabla}\xi}\right)_s, \qquad (13)$$

which leads to

$$\begin{aligned}
&\boldsymbol{\sigma} = \boldsymbol{\sigma}_e + \boldsymbol{\sigma}_\eta^{st} + \boldsymbol{\sigma}_\xi^{st}; \qquad \boldsymbol{\sigma}_e = (1-\phi(\xi))(K\varepsilon_{0e}\boldsymbol{I} + 2\mu \boldsymbol{e}_e); \qquad (14)\\
&\boldsymbol{\sigma}_\eta^{st} = (\psi^\nabla + \breve{\psi}_\theta)\boldsymbol{I} - \beta\sum_{i=1}^{n}(\boldsymbol{\nabla}\eta_i \otimes \boldsymbol{\nabla}\eta_i + b\boldsymbol{\nabla}\eta_i \otimes \sum_{j=1, i\neq j}^{n}\boldsymbol{\nabla}\eta_j);\\
&\boldsymbol{\sigma}_\xi^{st} = \psi_\xi \boldsymbol{I} - \beta_\xi \boldsymbol{\nabla}\xi \otimes \boldsymbol{\nabla}\xi = q(\eta_i)/\Delta_\xi\left(\left(16.62\xi^2(1-\xi)^2 + 0.542\Delta_\xi^2(\nabla\xi)^2\right)\boldsymbol{I} - 1.083\Delta_\xi^2 \boldsymbol{\nabla}\xi \otimes \boldsymbol{\nabla}\xi\right).
\end{aligned}$$

To obtain a stationary surface layer, $\xi = 1$ at the external surface and $\xi = 0$ at the distance of Δ_ξ from the surface and along the entire external surface are applied as the boundary conditions.

Material parameters. We will consider cubic-to-tetragonal phase transformation in NiAl alloy. We will use the following material parameters determined and/or collected from the literature in [4]:

$$A_0 = 4.40MPa\,K^{-1}, \quad \bar{A} = 5.32GPa, \quad \theta_e = 215\,K, \quad \theta_c = -183\,K, \quad a = 2.98,$$
$$B = 0, \quad D = 0.5GPa, \quad \beta = 2.59 \times 10^{-10}N, \quad L = 2596.5(Pa \cdot s)^{-1},$$
$$K = 112.62GPa, \quad \mu = 71.5GPa. \tag{15}$$

In our finite element method (FEM) simulations, the components of $\boldsymbol{\varepsilon}_t$ $(0.215, -0.078, -0.078)$ (for M_1) and $(-0.078, 0.215, -0.078)$ (for M_2) are used [4]. Also, $L_\xi = 30000(Pa \cdot s)^{-1}$, $\Delta\gamma = -0.4J/m^2$, and $b = 0.5$. Calculated width and energy of A-M interface for stress-free conditions are $\Delta_\eta = 1.5065nm$ and $E_\eta = 0.2245J/m^2$.

Problem formulation. The FEM code COMSOL was utilized for plane stress 2D problems. Rectangular $25 \times 12.5nm^2$ sample discretized with triangle Lagrange elements with quadratic approximation was treated. Length of the sample in the horizontal direction is not important as the same results were obtained after the length was doubled. All sides are stress-free, excluding zero vertical displacement at the upper and lower horizontal sides. Boundary conditions (8) for η_i for sharp interface were applied at the right vertical line only; for other sides, and for all sides for problems with surface layer, $q = const$ in Eq.(8). With a surface layer, a stationary solution for ξ was first obtained for $\eta_i = 0$, which was used as an initial condition. Without a layer, initial conditions are $\eta_i = 0.001$. The following models were considered: GL equation without mechanics; GL equations with mechanics, for $k = 1/3$, $2/3, 1$, with elastic properties independent of ξ and without surface stresses; the same with elastic properties dependent on ξ; and the same with surface stresses.

References

[1] V. I. Levitas and M. Javanbakht, Phys. Rev. Lett. **105**, 165701 (2010).

[2] V. I. Levitas and K. Samani, Nat. Commun. **2**, 284 (2011).

[3] Levitas, V.I., Preston, D.L., and Lee, D.-W., Phys. Rev. B **68**, 134201 (2003).

[4] V. I. Levitas and D. L. Preston, Phys. Rev. B **66**, 134206 and 134207 (2002).

Videos' descriptions

Video 1. Evolution of surface-induced nanostructure for coupled GL and mechanics equations with transformation strain $\boldsymbol{\varepsilon}_t$ and interface tension $\boldsymbol{\sigma}_\eta^{st}$ for $\overline{\Delta_\xi} = 0$ after critical nanostructure ($X_c = 0.6859$) loses its stability at slight increase in X ($X = 0.6864$).

Video 2. Evolution of surface-induced nanostructure for coupled GL and mechanics equations with transformation strain $\boldsymbol{\varepsilon}_t$ and constant elastic properties for $\overline{\Delta_\xi} = 0.066$ after critical nanostructure ($X_c = 0.6646$) loses its stability at slight increase in X ($X = 0.6658$).

Video 3. Evolution of surface-induced nanostructure for coupled GL and mechanics equations with transformation strain $\boldsymbol{\varepsilon}_t$ and constant elastic properties for $\overline{\Delta_\xi} = 0.199$ after critical nanostructure ($X_c = 0.6558$) loses its stability at slight increase in X ($X = 0.6563$).

Video 4. Evolution of surface-induced nanostructure for coupled GL and mechanics equations with transformation strain $\boldsymbol{\varepsilon}_t$ and constant elastic properties for $\overline{\Delta_\xi} = 0.332$ after critical nanostructure ($X_c = 0.6432$) loses its stability at slight increase in X ($X = 0.6445$).

Video 5. Evolution of surface-induced nanostructure for coupled GL and mechanics equations with transformation strain $\boldsymbol{\varepsilon}_t$ and constant elastic properties for $\overline{\Delta_\xi} = 0.465$ after critical nanostructure ($X_c = 0.6420$) loses its stability at slight increase in X ($X = 0.6432$).

Video 6. Evolution of surface-induced nanostructure for coupled GL and mechanics equations with transformation strain $\boldsymbol{\varepsilon}_t$, variable elastic properties and interface $\boldsymbol{\sigma}_\eta^{st}$ and surface $\boldsymbol{\sigma}_\xi^{st}$ tensions ($\boldsymbol{\varepsilon}_t$, $\phi(\xi)$, $\boldsymbol{\sigma}^{st}$) for $\overline{\Delta_\xi} = 0.199$ after critical nanostructure ($X_c = 0.6834$) loses its stability at slight increase in X ($X = 0.6859$).

Video 7. Evolution of surface-induced nanostructure for coupled GL and mechanics equations with transformation strain $\boldsymbol{\varepsilon}_t$, variable elastic properties and interface $\boldsymbol{\sigma}_\eta^{st}$ and surface $\boldsymbol{\sigma}_\xi^{st}$ tensions ($\boldsymbol{\varepsilon}_t$, $\phi(\xi)$, $\boldsymbol{\sigma}^{st}$) for $\overline{\Delta_\xi} = 1.66$ after critical nanostructure ($X_c = 0.8116$) loses its stability at slight increase in X ($X = 0.8141$).

Video 8. Evolution of surface-induced nanostructure for two martensitic variants for coupled GL and mechanics equations with transformation strain $\boldsymbol{\varepsilon}_t$ and constant elastic properties for $\overline{\Delta_\xi} = 0$ and $X = 0.7915$.

Video 9. Evolution of surface-induced nanostructure for two martensitic variants for coupled GL and mechanics equations with transformation strain $\boldsymbol{\varepsilon}_t$ and constant elastic properties for $\overline{\Delta_\xi} = 0.0166$ and $X = 0.7915$.

Video 10. Evolution of surface-induced nanostructure for two martensitic variants for coupled GL and mechanics equations with transformation strain $\boldsymbol{\varepsilon}_t$ and constant elastic properties for $\overline{\Delta_\xi} = 0.033$ and $X = 0.7915$.

Video 11. Evolution of surface-induced nanostructure for two martensitic variants for coupled GL and mechanics equations with transformation strain $\boldsymbol{\varepsilon}_t$ and constant elastic properties for $\overline{\Delta_\xi} = 0.133$ and $X = 0.7915$.